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MULTIPLET SEPARATIONS IN COMPLEX SPECTRA (OF d^3 AND d^1 CONFIGURATIONS)

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ABSTRACT. Expressions for multiplet separations derived by Goudsmit for complex spectra arising out of equivalent electron configuration have been applied to the spectra of vanadium and columbium, which have been recently analysed extensively on the basis of Zeeman effect and hyperfine structure studies. The check-up between theoretical and experimental values have indicated a correspondence chiefly in the case of the deeper terms. The disagreement in columbium II is exceptionally large.

INTRODUCTION

Separations between multiplet levels, in line spectra, were characterised according to Lande by factors, designated as Γ, giving the displacement of each level from the centre of gravity of the whole multiplet. They are similar to Lande's 'g' factors, explaining magnetic separations and can be represented thus

$$\Gamma = \Sigma a_i l_i s_i \cos(l_i s_i) \qquad \ldots \quad (1)$$

which gives the total interaction energy for several electrons. In the case of normal multiplets, the expression reduces to

$$\Gamma = A\cos(ls) = \tfrac{1}{2}A\{j(j+1) - l(l+1) - s(s+1)\} \qquad \ldots \quad (2)$$

where $$A = \Sigma a_i \frac{l_i}{l} \overline{\cos(l_i l)} \frac{s_i}{s} \overline{\cos(s_i s)},$$

is the well-known separation factor. For a given multiplet the Γ-values of the different levels may be calculated in terms of A with the help of the above equation. It gives us the Lande interval rule.

An interesting property of these Γ-factors is, as pointed out by Lande, that the sum of the Γ-values, for a given value of m, is the same for a strong as well as a weak field—known as the Γ-permanance rule. Goudsmit made a further investigation of the properties of these factors and following Pauli's study of the building up of the 'g' values of an atom from those of the individual electrons enunciated a Γ-sum-rule, analogous to the g sum-rule concerning Zeeman separations. It states that, for a number of levels arising from a given electron configuration, the sum of all the Γ-values belonging to a definite value of m, is independent of the strength of the field. This Γ-sum rule was illustrated by the case of two equivalent 'p' electrons. The Γ-sum remains constant for all couplings provided it is taken for these levels which have equal j's, among terms of a given configuration.

An important application of Goudsmit's rule is, as shown by him, that it is possible to derive expressions for multiplet separations in general cases.

Such expressions are of great practical value in the analysis of the structures of complicated spectra. The validity of the method was illustrated by Goudsmit (1928) (for levels arising from equivalent electrons) by a comparison of the observed and predicted multiplet separations chiefly in the spectrum of singly-ionised titanium which was then the only one of that type almost completely known.

Some other spectra corresponding to equivalents electron configurations have since been analysed, based extensively on evidence from Zeeman effect data and hyperfine structure observations and application of X-ray laws to iso-electronic systems and it would be of interest to examine how far predictions made on Goudsmit's method would be in accord with the actual analysis. Among the spectra considered in this paper are those due to d^3 and d^4 equivalent electron configurations, particularly of vanadium, columbium and chromium.

RESULTS AND DISCUSSION

TABLE I

Multiplet Separations for Equivalent d Electrons

Configuration	Multiplet	Total Separation	Separation factor, A
d^3	^{4}H	7 2a	1 3a
	^{4}P	1 5a	1 5a
	^{2}H	11/10a	1 5a
	^{2}G	27 2a	3 10a
	^{2}F	7 12a	1 6a
	^{2}D	5/6a	1 3a
	^{2}D		
	^{2}P	a	2 3a
d^4	^{5}D	5 2a	1 4a
	^{3}H	11/10a	1/10a
	^{3}G	27 20a	3 20a
	^{3}F	7 12a	1 12a
	^{3}F		
	^{3}D	−5/12a	−1/12a
	^{3}P	3/2a	1/2a
	^{3}P		

Table I is a part of the table derived by Goudsmit giving the total multiplet separations for equivalent d electrons (d^3 and d^4) expressed in terms of 'a'. It also gives the values of the separation factor Λ. For the method of deriving these values, reference may be made to Goudsmit's original paper (1928).

A notable feature in the table is the predicted inversion of the two terms (d^4) ^{2}F and (d^4) ^{3}D, for which the separations are negative.

Table II gives the observed and calculated multiplet separations in the iso-electronic spectra Ti II, (Bacher and Goudsmidt, 1932) V III, and Cr IV (Bowen, 1937) and in Zr II, for which the ground configuration corresponds to d^3. In each case the constant 'a' is estimated from the ^{2}H separation,

TABLE II

Separations in Spectra of d^3 Configuration

Term	Spect.	j = 5½ obs	5½ calc	4½ obs	4½ calc	3½ obs	3½ calc	2½ obs	2½ calc	1½ obs	1½ calc	½ obs	½ calc	Over-all separation obs	Over-all separation calc
	Ti II			128·4	133·2	103·1	103·6	75·5	71·1					307·6	310·9
^{4}P	V III			244	211	194	165	145	117					583	493
	Cr IV			396	345	310	268	237	192					949	805
	Zr II			458·0	511	401·0	398	322·8	284·0					1185·4	1193
	Ti II							122·3	71·1	37·1	11·1	154·1		118·5	
^{4}P	V III							181	118	77	21	258		188	
	Cr IV							290	192	119	115	418		307	
	Zr II							189·7	84	45·9	16·1	115·0		451·7	
	Ti II	97·8	97·8												
^{2}H	V III	155	155												
	Cr IV	253	283												
	Zr II	375·2	375·2												
	Ti II			130·5	124·1										
^{2}G	V III			22·	192										
	Cr IV			349	311										
	Zr II			315·1	401·7										
	Ti II					−50·0	−51·8								
^{2}F	V III						−82								
	Cr IV						131								
	Zr II					−81·0	−109								
	Ti II							120·4							74·1
^{2}D·S	V III							147							123
	Cr IV							−						—	192
	Zr II							734·4						1169·1	284
										1250	88·9				
^{2}P										180	141				
										—	230				
										466·8	341				

the term having the largest l value. For instance for V III, d^1 $^2H \rightarrow 11a/10 = 155$ or $a = 140.9$. Hence the predicted overall separation for d^1 $^4F = 7a/2 = 493$. The component separations are then

$$^1F_{3\frac{1}{2}} - {}^1F_{4\frac{1}{2}} = 211$$

$$^1F_{2\frac{1}{2}} - {}^1F_{3\frac{1}{2}} = 165$$

$$^1F_{1\frac{1}{2}} - {}^1F_{2\frac{1}{2}} = 117$$

The other term separations are similarly calculated.

The agreement is good in certain cases chiefly in terms of higher l and J values. The largest deviations are in the ^1P and ^2P intervals. The higher stage iso-electronic spectra also indicate considerable departures. In general it is the overall separations, rather than the component intervals that give better agreement. Such disagreement may be partly due to the departure from the Russel-Saunders type of coupling.

TABLE III

Separations in Spectra of d^1 Configuration

Term	J=6 Spectrum	5 obs	5 cal	4 obs	4 cal	3 obs	3 cal	2 obs	2 cal	1 obs	1 cal	0 obs	0 cal	Overall Separations obs	Overall Separations cal
	V II					130 3	146 4	102 5	109 8	70 6	73 2	36 1	36 6	339 3	366 0
^3D	Cr III					220	236 4	172	177 3	118 0	118 2	60	59	572	591
	Cb II					423 5	615 2	363.6	161 4	279 4	307 6	150	153 8	1221 9	1538 3
	V II	84.6	87.6	76 4	73 0									161 0	161 0
^3H	Cr III	136	142	124	118									260	260
	Cb II	373 9	369.1	302 9	307 4									676 8	676 8
	V II			99 5	109.5	94 1	87.6							193 9	197 1
^3G	Cr III			142	177	160	142							292	319
	Cb II			314.2	462	357 2	369 6							671 4	831 6
						66 3		51 8							
	V II					12 2		39 9						176 2	85 4
^1D's	Cr III					72		60						—	138
	Cb II					355 1		459 6						1574.1	359 1
						-24 5		88 1 2							
	V II														
^3D	Cr III							60	-219	21 3	116			84 3	-305
	Cb II								-355		236				591
								-424 8	154.5	360 9	-102.6			-63 9	-256.5
	V II									393 5		219 3		233.6	219 6
^3P's	Cr III									-258 4		-120.8			
	Cb II									68		—			354.6
										1069.0		-			
										-512.0		630 1		979.9	923.0
												-207 2			

The inversion of the ^1F term in Ti II and Zr II are noteworthy ; a similar inversion in V III and Cr IV spectra may be confidently predicted.

The largest discrepancy in the ^2D interval sum of Zr II is 1169.1, as observed against a calculated sum of 284. Even the order of magnitude is very high. Perhaps the identification of the terms is uncertain.

Table III gives the results for the spectra of V II, (Meggers and Moore, 1940) Cr III (Bowen, 1937) and Cb II, (Humphrey and Meggers, 1948) corresponding to the d^1 configuration. Of these the analysis of V II and Cb II was carried out very extensively and based on evidence derived from the study of the hyperfine structure and Zeeman effect of a large number of lines. The agreement between the observed and calculated separation is close, for ^1D and ^3G levels of V II and Cr III and in particular of the overall intervals ; Cb II intervals show generally much larger deviations. For ^1F and ^3P, theory can predict only the sum of the intervals of each type of term, *i. e.*, Σ F and not of the terms separately. In V II the observed values for ^3F's is double the calculated value and the discrepancy is much larger for Cb II. The ^1P sum is consistent both for V II and Cb II, as well as the inversion of the ^3D term in Cb II. The identification of ^1D in V II may be uncertain.

From the foregoing study it would seem that the method of Goudsmit may well be taken recourse to in predicting the interval sums with a certain confidence only for the deeper set of terms of a given configuration.

The data for the various spectra referred to above are taken from the following references.

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REFERENCES

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